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14. ABSTRACT
Direct absorption IR and LIF methods developed under AFOSR support have been used to study state-to-state inelastic and reactive scattering dynamics under single collision conditions. Efforts over the last three years have led to significant achievements in several areas, highlighted by 21 publications published, in press or submitted to the high profile scientific journals. These milestones include: 1) Rovibrationally quantum state-resolved collision dynamics of F atoms with H2O and HCl in crossed molecular expansions, 2) Polarization modulation studies of quantum state resolved stereodynamics for hyperthermal CO2 collisions at the gas-liquid interface, 3) Correlated angular and quantum state resolved studies of hyperthermal gas-liquid scattering, 4) Large scale dynamical trajectory simulations for theoretical analysis of the gas-liquid scattering studies, 5) State-resolved reactive scattering of F atoms at hydrocarbon liquid surfaces, 6) Studies of state-resolved energy transfer with electron-hole pair formation.

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AFOSR Progress/Evaluation report: 9/1/06

State-to-State Thermal/Hyperthermal Collision Dynamics of Atmospheric Species

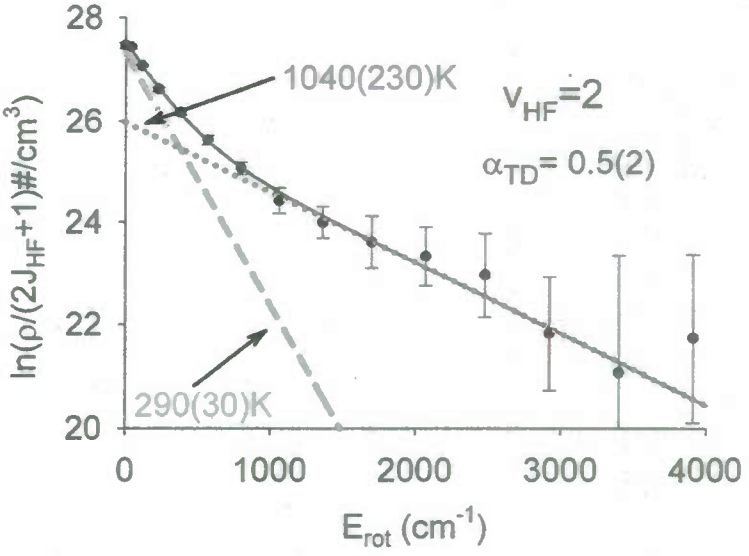
Abstract: Status of effort

Direct absorption IR laser methods developed under AFOSR support have been used to study state-to-state inelastic and reactive scattering dynamics under single collision conditions. Efforts over this past year have led to significant progress in multiple key areas: i) Inelastic scattering dynamics of jet cooled hyperthermal CO_2 via collisions at the gas-liquid interface, ii) State resolved reactive scattering dynamics of H abstraction and HF(v,J) formation by F atom collisions with liquid squalane, iii) Full adiabatic and non-adiabatic potential energy surface calculations (at the complete active space/multireference configuration interaction level) for benchmark F + HCl → HF(v,J) + Cl reaction dynamics, and iv) Construction of a new experimental apparatus for velocity map ion imaging of reactive scattering dynamics.

Accomplishments/New Findings

The program has multiple projects currently operating in a highly research productive mode. Three selected highlights from these projects over the past year are reported below.

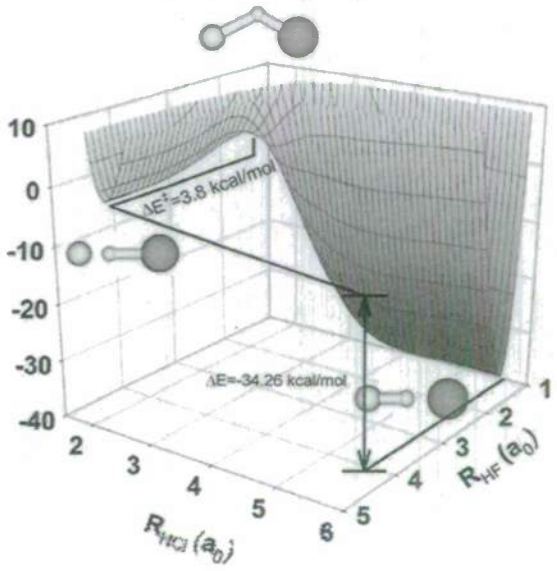
1) The past many years have witnessed detailed scattering studies performed between high energy molecular beams and low vapor pressure liquid surfaces, such as large chain hydrocarbons,[1-3] perfluoropolyethers (PFPE),[4] and even liquid metals,[5,6] based on translational energy loss time of flight mass spectrometry. It has proven far more challenging, however, to investigate *internal* rovibrational degrees of freedom in gas-liquid energy transfer dynamics.[7,8] As a new thrust over this granting period, we have constructed an apparatus for detailed study of both inelastic and reactive energy transfer dynamics at the gas-liquid interface, with full quantum state-resolution of the nascent internal states.[9] The approach relies on supersonic jet-cooled molecular beams impinging on a continually renewable Fenn-type[10]



liquid surface in vacuum, exploiting sub-Doppler diode laser absorption methods to probe *rotation, vibration and translational* distributions in the scattered flux.

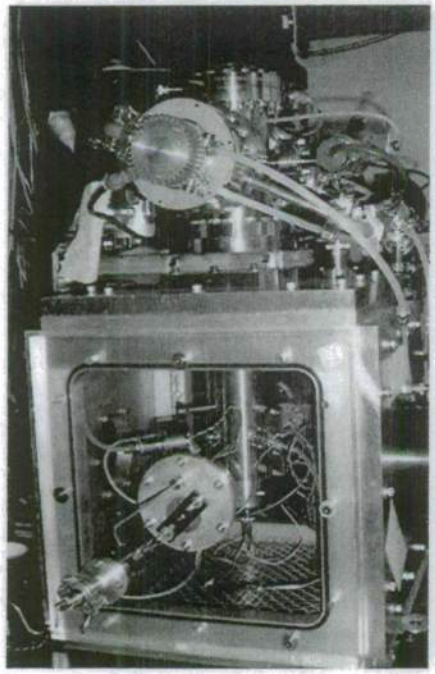
As the most recent example of these efforts, exothermic reactive scattering of F atoms at the gas-liquid interface of a liquid hydrocarbon (squalane) surface has been studied under single collision conditions by shot noise limited high-resolution infrared absorption on the nascent HF(v,J) product. The nascent HF(v,J) vibrational distributions are inverted, indicating insufficient time for complete vibrational energy transfer into the surface liquid. The HF(v=2,J) rotational distributions are well fit with a two temperature Boltzmann analysis (see above), with a near room temperature component ($T_{TD} \approx 290$ K) and a second much hotter scattering component ($T_{HDS} \approx 1040$ K). These data provide novel quantum state level support for *microscopic branching* in the atom abstraction dynamics corresponding to escape of nascent HF from the liquid surface on time scales both slow and fast with respect to rotational relaxation.

2) There is a strongly growing interest in the role of multiple potential energy surfaces and *non-adiabatic* dynamics for chemical reactions in the upper atmosphere. As a simple but challenging benchmark system for such dynamics, we have developed high level electronic potential energy surfaces for the $F(^2P) + HCl \rightarrow HF + Cl(^2P)$ reaction. The *ab initio* calculations are done at the multireference configuration interaction + Davidson correction (MRCI+Q) level of theory by complete basis set extrapolation of the aug-cc-pVnZ (n=2,3,4) energies. Due to low-lying charge transfer states in the transition state region, the molecular orbitals are obtained by 6-state dynamically weighted multichannel self consistent field (DW-MCSCF) methods. Additional perturbative refinement of the energies is achieved by implementing simple one-parameter correlation energy scaling to reproduce the experimental exothermicity ($\Delta E = -33.06$ kcal/mol) for the reaction. *Ab initio* points are fit to an analytical function based on sum of 2- and 3-body contributions, yielding an RMS deviation of < 0.3 kcal/mol for all geometries below 10 kcal/mol above the barrier. Of particular relevance to non-adiabatic dynamics, the calculations show significant multireference character in the transition state region, which is located 3.8 kcal/mol with respect to F + HCl reactants and features a strongly bent F-H-Cl transition state geometry ($\theta \approx 123.5°$). Finally, the surface also exhibits two conical intersection seams that are energetically accessible at low collision energies. These seams arise naturally from allowed crossings in the $C_{\infty v}$ linear configuration that become avoided in C_s bent

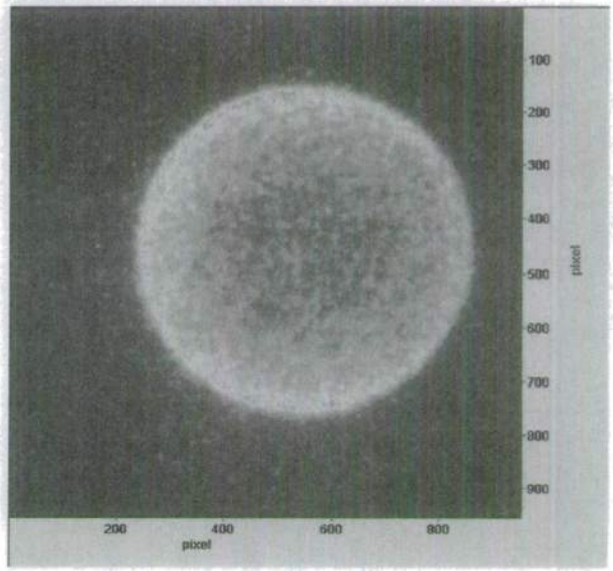


configurations of both the reactant and product, and should be a hallmark of all X-H-Y atom transfer reaction dynamics between (^{2}P) halogen atoms.

3) For further investigation of non-adiabatic dynamics in these simple reaction systems, we are upgrading the laser detection sensitivity to ion counting. Thus, as a new building thrust, we have begun converting the F-center laser spectrometer system over to a REMPI based ion imaging apparatus. The vacuum chamber is now configured to allow two



pulsed supersonic beams to enter via skimmers mounted directly onto a central differentially pumped time of flight tube (see figure). In addition, we have windows to introduce a tunable frequency tripled UV laser for state resolved REMPI tagging of either product or reactant species in the jet intersection region. The ions are then accelerated onto a microchannel plate and phosphor screen assembly by a -1800 V repeller voltage in a standard velocity map imaging configuration. The individual ions are then detected and stored by CCD camera acquisition and analyzed with fast centroiding algorithms. This system will soon be used to study reactive scattering of F + HCl, where the differentially resolved, fully correlated final Cl spin orbit state and HF(v,J) rovibrational distributions will be obtained via ion velocity map imaging. As a "warm up", sample data indicating the current status of the system is shown in the figure below, which represents nascent Cl recoil velocity distributions due to photolysis of Cl_2 at 353 nm, with the Cl($^2P_{3/2}$) lower spin orbit state selectively detected by resonant 2+1 photoionization by a 235 nm laser entering from the right and a supersonic Cl_2 beam entering from the lower left. The bright "ring" reflects a nearly isotropic Cl recoil distribution with β close to zero. The displacement of the ring center with respect to the flight tube axis is due to initial velocity of the Cl_2 expansion in the lab frame. The lack of perfect right-left symmetry in the image is due to blue and red shifting of the photolytic Cl atom absorption frequency, which arises since the UV laser resolution is already narrower than the recoil Doppler width.



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Personnel Supported:

1) Erin Whitney (graduate student)
2) Tom Baker (graduate student)
3) Alex Zolot (graduate student)
4) Brad Perkins (graduate student)
5) Michael P. Deskevich (graduate student)
6) Oliver Monti (postdoctoral student)

Papers published or submitted in 2005-2006 acknowledging AFOSR support:

S. A. Nizkorodov, M. Ziemkiewicz and D. J. Nesbitt, "Vibrationally-mediated dissociation of H_2O dimer and Ar-H_2O in the v_{OH}=2 manifold," J. Chem. Phys. 122, 194316-194327 (2005).

E. S. Whitney, A. M. Zolot, A. B. McCoy, J. Francisco and D. J. Nesbitt, "Impulsive model scattering dynamics in atom + polyatomic systems: $F + C_2H_6 \rightarrow HF(v,J) + C_2H_5$," J. Chem. Phys. 122, 124310-124320 (2005).

F. Dong, D. Uy, S. Davis, M. Child and D. J. Nesbitt, "Molecular ions in a slit-jet discharge: High-resolution infrared spectroscopy and tunneling dynamics of HD_2O^+," J. Chem. Phys. 122, 224301-224314 (2005).

M. P. Deskevich and D. J. Nesbitt, "Large amplitude quantum mechanics in polyatomic hydrides: I. Particles-on-a-Sphere model for XH_n," J. Chem. Phys. 23, 84304 (2005).

B. G. Perkins, Jr., T. Haeber and D. J. Nesbitt, "Inelastic energy transfer dynamics at the gas-liquid interface: High resolution IR diode laser studies of quantum state-resolved CO_2 scattering from polyfluorophenyl ether (PFPE)", J. Phys. Chem. B 34, 16396-16405 (2005)

M. Ziemkiewicz, M. Wojcik and D. J. Nesbitt, "Direct evidence for non-adiabatic dynamics in atom + polyatom reactive scattering: F + $D_2O \rightarrow$ DF + OD," J. Chem. Phys. 123, 224307 (2005).

M. Y. Hayes, M. P. Deskevich, D. J. Nesbitt, K. Takahashi and R. T. Skodje, "A simple picture for the rotational enhancement of the rate for the F + HCl $\rightarrow$ HF + Cl reaction: A dynamical study using a new *ab initio* potential energy surface", J. Phys. Chem. A 110, 436-444 (2006).

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M. P. Deskevich, M. Y. Hayes, K. Takahashi, R. T. Skodje and D. J. Nesbitt, "Multireference configuration interaction calculations for the F(^{2}P) + HCl $\rightarrow$ HF + Cl(^{2}P) reaction: A correlation scaled ground state (1^2A') potential energy surface", J. Chem. Phys. 124, xxx (2006).

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A. M. Zolot, B. G. Perkins, W. W. Harper, P. J. Dagdigian, and D. J. Nesbitt, "Quantum-state resolved reaction dynamics at the gas-liquid interface: Direct absorption detection of HF(v,J) product from F(^{2}P) + Squalane", J. Chem. Phys. 124, xxx (2006).

F. Dong and D. J. Nesbitt, "Jet-Cooled spectroscopy of H_2DO^+: Barrier heights and isotope-dependent tunneling dynamics from H_3O^+ to D_3O^+", J. Chem. Phys. 125 (in press).

Interactions/Transitions:

Invited talks in 2004-2005 acknowledging AFOSR support:

"From Confocal Fluorescence to Photoionization Microscopy of Nanostructures," 229th National ACS Meeting, San Diego, CA, March 15, 2005.

"Time Dependent Fluorescence and Blinking Dynamics in Semiconductor Quantum Dots," ACS 229th National Meeting, San Diego, CA, March 17, 2005.

"Reaction Dynamics with Quantum State Resolution: Finding the Physics Behind the Chemistry", Department of Chemistry, Wayne State University, Detroit, MI, March 23, 2005.

"Fluorescence Studies at the Single Molecule Level: From Quantum Dot Blinking to RNA Folding", Single Molecule Workshop, U. S. Department of Energy, Rockville, MD, April 11, 2005.

"Optical Physics at the Single Molecule Level: From Quantum Dots to Docking of RNA" , Lehrstuhl für BioMolekulare Optik, Department für Physik, Ludwig Maximilians Universität, München, Germany, April 12, 2005.

"Dynamics with Quantum State Resolution: Finding the Physics Behind the Chemistry," Department of Theoretical and Physical Chemistry, Universitaet Stuttgart, April 19, 2005.

"Time Dependent Fluorescence and Blinking Dynamics in Semiconductor Quantum Dots," Los Alamos National Laboratory, June 17, 2005.

"Spectroscopy on a Mission: Reaction Dynamics and Highly Reactive Chemical Intermediates," 60th International Symposium on Molecular Spectroscopy, Columbus, OH, June 20, 2005.

"Molecular Splashes and Molecular Pretzels", Physical and Theoretical Chemistry Laboratory, Oxford University, Oxford, UK, July 20, 2005.

"Landscapes in elementary F + diatom and triatom reactions: Potential surfaces and state-resolved experiments", ACS 230th National Meeting, Washington, DC, August 30, 2005.

"Long range electron ejection dynamics in quantum dots: To blink or not to blink", ACS 230th National Meeting, Washington, DC, August 31, 2005.

"Spectroscopy and Dynamics of Jet-Cooled Molecular Transients", 28th International Symposium on Free Radical, Leysin, Switzerland, September 8, 2005.

"Hydrogen Bonding, Spectroscopy and Dynamics: From H_3O^+ to RNA", International Union of Pure and Applied Chemistry", Pisa, Italy, September 9, 2005.

"Spectroscopy One Molecule at a Time: From RNA Folding to Quantum Dots", Department of Chemistry, University of Puerto Rico-Mayaguez, October 13, 2005.

"Spectroscopy One Molecule at a Time: From RNA Folding to Quantum Dots", Department of Chemistry, University of Puerto Rico-Rio Piedras, October 14, 2005.

"Spectroscopic Windows into Chemical Dynamics: Jet Cooled Radicals, Bouncing Molecules and Photoionization Microscopy", 53rd Western Spectroscopy Association, Asilomar, CA, February 1, 2006.

"From Splashing Molecules at the Gas-liquid Interface to Single RNA Folding Kinetics", Department of Chemistry and Biochemistry, Montana State University, Bozemann, MN, February 10, 2006.

"Intramolecular Dynamics in Molecular Ions: A High Resolution Perspective, Molecular and Ionic Clusters Gordon Conference, Ventura, CA, February 22, 2006.

"Chemical Physics at the Single Molecule Level: From Quantum Dots to Docking of RNA", Department of Chemistry, University of Rochester, Rochester, NY, March 8, 2006.

"Fluorescence Kinetics in Nanoscale Systems", American Physical Society Meeting. Physical Chemistry of Nanoscale Systems, Baltimore, MD, March 13, 2006.

"Collisions at gas-liquid interfaces: "Splashing" molecules with quantum state resolution", 231st National Meeting, American Chemical Society, Atlanta, GA, March 27, 2006.

"Splashing molecules with quantum state resolution", Lehrstuhl fuer BioMolekulare Optik, Department of Physics, Ludwig Maximilians Universitaet, Munich, Germany, April 25, 2006.

"Gas-Liquid Interfaces and RNA Folding: Single Collisions to Single Molecules", Department of Chemistry and Biochemistry, U. C. Berkeley, Berkeley, CA, May 16, 2006.

"Quantum State Resolved Reaction Dynamics: From the Gas Phase to the Gas-Liquid Interface", Molecular Dynamics Contractors Meeting, Air Force Office of Scientific Research, Arlington, VA, June 5, 2006

"Probing Structure and Dynamics: An Overview of Vibrationally Driven Reactions", Gordon Conference on Vibrational Spectroscopy, Biddeford, ME, July 5, 2006

Consulting/Advisory Functions:

Advisory interactions with colleagues at Air Force Research Laboratory (Dr. James Dodd, Dr. Steve Lipson) regarding their radical kinetics program relevant to "airglow" in the upper atmosphere.

Visit to Kirtland Air Force Base and advisory interactions with members of the Advanced Research Lab (David (Tony) Hostutler and Gerry Manke). Discussed ways of improving operating pressures and efficiencies for production of $O_2(^1\Delta)$ with alternative slit discharge sources.

Interactions with Lt. Col Michael (Jeff) Salyards at Air Force Academy, Colorado Springs, regarding undergraduate chemical physics education and research opportunities

Extensive scientific interactions with Paul Dagdigian during a 6 -month sabbatical Visiting Fellowship here at JILA (Fall 2005). In particular, he has helped us implement an ion imaging system for reactive scattering studies.

Advisory committee, Molecular Spectroscopy Symposium (1995-present), Advisory committee, International Meeting on Near Field Optics (2000-present), Organizer for the OSA-ILS symposium on single molecule detection/near field imaging,

ACS Chair Nominations Committee (2006)
ACS Chair for Physical Chemistry (2005)
ACS Program Committee member for Physical Chemistry (2000-05)
Editorial Board, Journal of Chemical Physics
Editorial Board, Journal of Physical Chemistry
Editorial Board, Molecular Physics
Editorial Board, Chemical Reviews
Regional Editor, Physical Chemistry Chemical Physics

Inventions and Patent disclosures:
None

Honors, Awards or Fellowships received (2004-2005)
Alexander von Humboldt Fellowship, Humboldt Foundation
American Physical Society Fellow
Editorial Board, Molecular Physics
Editorial Board, Chemical Reviews
National Institute of Standards and Technology Fellow, 2005
Fellow of the Royal Society of Chemistry (UK), 2005